

SCIENCE FOR GLASS PRODUCTION

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EFFECT OF THE OXIDATION – REDUCTION POTENTIAL ON THE PRONENESS OF GLASS TO FORM BUBBLES

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The fining of glass is closely related with the oxidation-reduction potential of the glass, which is determined by means of an indication index — the fraction of bivalent iron, which is proportional to the absorption of the glass in the range 900 – 1100 nm. The appearance of seeds in optical glasses is explained by elevated solubility of nitrogen in the molten glass with an elevated reduction potential. Admixing cullet which possesses a reducing potential and vice versa destroys the solubility of sulfur in the molten glass and increases the risk of the appearance of seeds and foaming of the molten glass.

Key words: oxidation-reduction potential, fining of glass, seed, foaming of molten glass.

Oxidation-reduction processes occurring in the production of building materials (glass, ceramic, cement) and articles made from them have a fundamental effect on the quality of the finished product.

One of the criteria for competitiveness is the external appearance, which is largely determined by an article's color. Predominately mineral raw materials, more or less contaminated with coloring impurities — compounds of iron, titanium, manganese, chromium, and others, which impart to a product a unique and unattractive color, are used in the production of silicate building materials. Technological techniques involving the regulation and control of the oxidation – reduction processes are widely used to improve this situation, specifically, to whiten ceramic and cement and to decolorize glass [1 – 7].

Oxidation-reduction equilibria are also the basis for fining any kind of glass — optical and special purpose — where the system As_2O_3 (Sb_2O_3) + nitrate is used and construction and container glass fined by means of the composition Na_2SO_4 + carbon [8].

The bubbles in glass come from gases which are released, when the mix is poured, from pores of the refractory material lining the glassmaking furnace as a result of corrosion and enter the melt from the atmosphere in the furnace. Physical and chemical solubility of gases are distinguished. The gases which are inert with respect the molten glass (for

example, inert gases) dissolve physically; water vapor, hydrogen, CO_2 , and SO_2 dissolve predominately chemically; the character of the solubility of oxygen depends on the presence of multivalent ions in the melt and that of N_2 depends on the oxidation – reduction conditions of glassmaking [9, p. 166].

The physical and chemical solubility of gases is a function of the composition of the glass (specifically, the concentration and nature of the modifying ion, and so on) and at the same time the oxidation-reduction conditions of glassmaking. On the other hand, the formation of the glass with a concrete value of the oxidation-reduction potential (ORP) is determined predominately by the acid-base properties of the matrix and the oxidation-reduction conditions of glassmaking and extraction. For this reason, it can be expected with high probability that the capability of the melt to undergo fining as well as secondary release of bubbles with subsequent high-temperature industrial processing are inherited from the ORP.

The objective of the present work is to analyze the effect of the oxidation-reduction potential of glass on the proneness of the glass to form bubbles and foam up.

Optical colorless alkali-boro-silicate crown and container glasses — colorless (white), green, and brown — were chosen for the present investigations.

Table 1 gives the content of H_2O , $\text{CO} + \text{CO}_2$, N_2 , H_2 , and O_2 in the alkali-boro-silicate crown glass, made under laboratory conditions in an air atmosphere from conventional and sol-gel mixes.

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TABLE 1. Results of Gas Analysis of Alkali-Boro-Silicate Crown Glass Made from Conventional and Sol-Gel Mixes*

Mix used for glassmaking	Temperature, °C	Pressure, Pa				
		H ₂ O	CO + CO ₂	N ₂	H ₂	O ₂
Conventional**	840	808	117	19	92	0.7
	940	4529	125	19	97	0.7
	1100	9405	95	25	93	Traces
Sol-Gel***	840	680	146	118	12	1
	940	4109	102	137	12	2
	1090	8087	68	146	13	3

* Fining agents were not used.

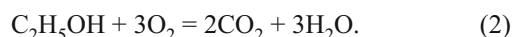
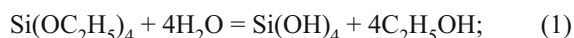
** Alkali and alkali-earth metals were introduced predominately by means of carbonates.

*** Alkali and alkali-earth metal introduced by means of nitrates.

It is well known that the preparation of the conventional mix reduces to mixing in definite proportions powdered initial materials of natural (for noncritical construction and container glass) and artificial (for optical, special, and certain other types of glass) origin. In the present work a sol-gel mix (SGM) was obtained by acidic hydrolysis of silicon alkoxide (tetraethyl ether of orthosilicic acid — TEOS — $\text{Si}(\text{OC}_2\text{H}_5)_4$) by means of a water solution containing all other components of the glass. The sol prepared thickened during aging or careful heating, converting into a gel which was further dried, heat-treated to a powder state, and used for glass-making. The ORP was evaluated using an indication index of the basicity level — the fraction of Fe^{2+} [4], which in a sol-gel is much higher than in glass made from the conventional mix: 12.5 and 4.3%, respectively. We shall examine the reasons for this phenomenon.

The gas analysis was performed at the Scientific – Research Technological Institute of Optical Materials Science at the All-Russia Science Center S. I. Vavilov State Optical Institute. The essence of the method consists in heating pre-evacuated glass to a fixed temperature followed by measurement of the partial pressure of the gases released and determining their composition chromatographically.

The amount of dissolved water in $\text{CO} + \text{CO}_2$ in both glasses is practically identical, though the sol-gel mix was synthesized in a water solution whose solid phase content is limited by the solubility of boric acid about 4 g in 100 g H_2O [10], while theoretically in the course of the hydrolysis of silicon alkoxide via the reaction (1) and subsequent heat-treatment of the sol-gel product to a powder state according to the reaction (2) 3 – 4 times more CO_2 is released than with the decomposition of carbonates from which the conventional mix is obtained:



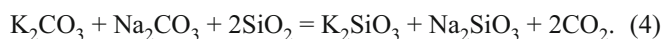
Evidently, a large fraction of the water and carbon oxides from the sol-gel product is removed at the stage where the product is dried and heat-treated.

The insensitivity of the carbon oxides and water to the form of the mix from which the glass is made can be explained by the fact that other conditions being equal the solubility of these gases depends largely on the basicity, i.e. the concentration of uni- and bivalent oxides in the glass [9], which in the case studied is the same.

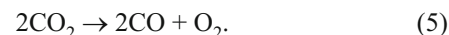
The appearance of hydrogen can be explained by the thermal dissociation and interaction of the gases released when the conventional mix is heated; the carbonates (with the exception of alkali) decompose into metal oxide and CO_2 . The acids and bases form water vapor, for example [10, 11]



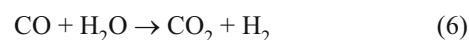
Silicate formation in potassium-sodium-silicate glasses is accompanied by the release of carbon dioxide gas according to the reaction [8]



At 1000°C 99.3% of the CO_2 dissociates [12]



Strong reducers can form as a result of the interaction of gaseous products with one another. Hydrogen can appear at 700°C [12]. This is recorded by the results of gas analysis of the glass obtained from a conventional mix:



The 7 – 8 fold decrease of the partial pressure (and of the associated concentration) of hydrogen in glass obtained with ZGM is partially explained by the absence of carbonates (see note in Table 1).

The solubility of nitrogen in melt obtained from the sol-gel product is 6 – 7 time higher and is associated with the elevated concentration of nitrogen-containing compounds (see note in Table 1) as well as with the high reduction potential of the SGM, which is a result of the incomplete oxidation of the carbon-containing compounds formed during the hydrolysis of the silicon alkoxide according to the reactions presented. The SGM partially melts during heat-treatment; this prevents oxygen in the air from flowing into the interior volume of the material and full oxidation. This is the reason for the elevated reduction potential of the glass obtained from the sol-gel product.

According to the data of [9, 13, 14] the physical solubility of nitrogen in lime-sodium glass after 16 hours of swirling at 1400°C is 4.2×10^{-4} vol.%, while under reduction conditions, when nitrogen interacts chemically with the melt its concentration increases $10^4 - 10^5$ fold — to 0.5 wt.%. In all probability, the identical phenomenon is responsible for the elevated content of nitrogen in the glass obtained from SGM.

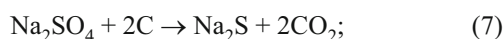
As a result, the number of bubbles in the more reduced sol-gel glass made in air is 1 – 1.5 orders of magnitude greater than when conventional materials are used.

Manufacturers of container glass use in the technological process imported cullet which often differs from the glass produced at the plant not only in composition but also color and hue. The entry into the furnace of substantial amounts of cullet with alien colors is fraught not only with an inadmissible change of the regular color characteristics of the product but also the appearance of bubbles, seeds, mass rejects, and in the case of strong foaming stopping of extraction and complete or partial discharge of the molten glass from the furnace.

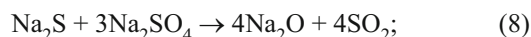
The system sodium sulfate + carbon is used to fine container glass. The carbon is introduced into the mix in the amount 5% of the carbon mass in order to accelerate glassmaking and decomposition of Na_2SO_4 [15].

The basic oxidation-reduction interactions accompanying the decomposition of sodium sulfate during glassmaking are characterized by the following reactions [9]:

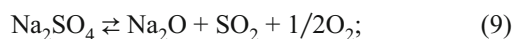
partial reduction of Na_2SO_4 to sulfide (740 – 800°C):



oxidation of Na_2S by excess Na_2SO_4 :



decomposition of sodium sulfate as a result of thermal dissociation:



silicate formation:

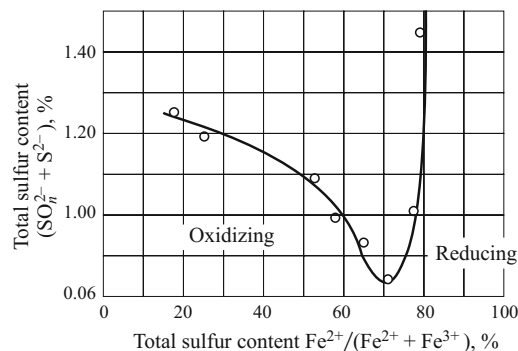
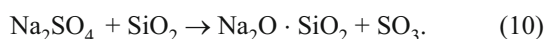
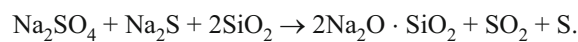


Fig. 1. Sulfur solubility versus the oxygen partial pressure.

The remaining sulfate in the melt (0.2 – 0.6 wt.%) acts as a weak oxidizer in accordance with the transition

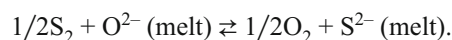


In the presence of reducing additives in the mix (for example, sulfate and carbon or sulfate and sulfide) the following reaction which proceeds at temperatures above 860°C is added to the release of SO_2 (9) which starts during the primary melting:



Subsequent dissolution of the sulfur depends on the oxygen partial pressure, i.e., oxidation-reduction conditions of glassmaking.

For reducing conditions sulfur replaces O^{2-} in the form S^{2-} :



For more oxidative conditions sulfur in the form SO_4^{2-} becomes incorporated in the glass:



The solubility of sulfur in the melt changes in accordance with Fig. 1 (taken from [9], p. 177): the SO_4^{2-} concentration is directly proportional and S^{2-} inversely proportional to the oxygen pressure p_{O_2} . The fraction of bivalent iron in the glass was used as the p_{O_2} indicator.

Hence it is evident that sudden oscillations of the oxidation-reduction conditions caused by, among other things, alien-colored cullet with a substantially different ORP entering the furnace change the solubility of sulfur and can result in the formation of seeds [9, p. 202].

The oxide composition of the container glasses studied is very close. The density (method of hydrostatic weighing in distilled water) differs negligibly: white — 2.47 g/cm³; green — 2.48 g/cm³; brown — 2.49 g/cm³.

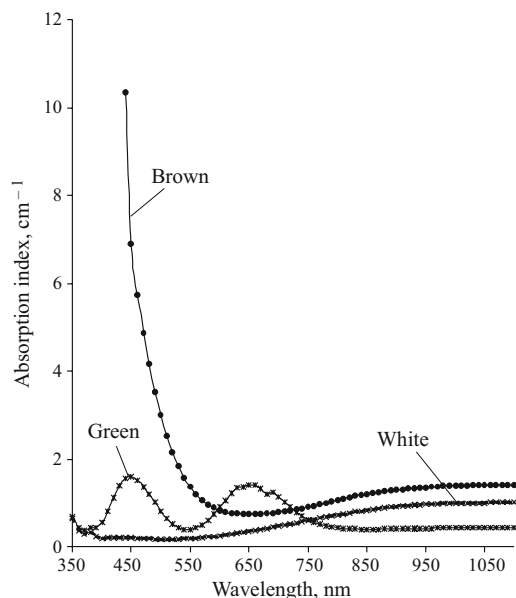


Fig. 2. Spectral curves of the absorption indices of container glass. The color of the glass is indicated on each curve.

The spectral absorption indices a_{λ} of all glasses in the wavelength range 350 – 1100 nm were calculated using the expression (13):

$$a_{\lambda} = \frac{-\log \tau_{\lambda}}{l}, \quad (13)$$

where τ_{λ} is the coefficient of light transmission of the glass at wavelength λ (fractions of 1) and l is the thickness of the glass sample, cm. The curves are presented in Fig. 2.

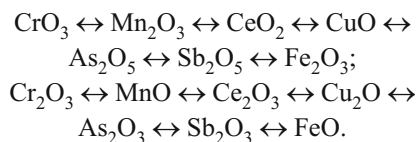
Coloring agents, as such, are not added to white container glass. Light-blue glass is created by added iron in form Fe^{2+} with absorption band near 1000 – 1100 nm which enters from the raw materials. Green color is due to the presence of chromium in the form Cr^{3+} (the absorption maxima in the bands 460 and 560 nm), added as a component into the mix.

TABLE 2. Composition of Mixes

Mix No.	Cullet content in mix, wt. %		
	Green (G)	White (W)	Brown (B)
1	100	0	0
2	0	100	0
3	0	0	100
4	90	10	0
5	90	0	10
6	75	25	0
7	75	0	25
8	50	50	0
9	50	0	50
10	0	50	50

Finally, the brown color, which is due to an amber chromophore with a very strong absorption band near 410 nm, arises under sharply reducing conditions. It is affected by the content of iron, sulfur compounds, and reducing agents (carbon) [9]. A brown chromophore is created by the ion Fe^{3+} , surrounded by three or fewer O^{2-} ions and one or more S^{2-} ions in tetrahedral coordination.

It is evident from Fig. 2 that at wavelengths 1000 – 1100 nm the absorption index of white glass and therefore the concentration and fraction of bivalent iron in it are much greater than in green glass. Since natural raw materials with quite close content of impurity iron is used to make container glass, the effect of a decrease of the content of its oxide form in green glass can be explained solely by the influence of chromium, which oxidizes iron to Fe^{3+} in accordance with the Weil series [16]. Each oxide on the left with a higher valence form oxidizes any oxide lying on the right and in a state of lower valence:



For this reason it can be supposed that the equilibrium $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ in white glass is shifted farther to the left as compared with green glass, and therefore in accordance with [4] its reduction potential is somewhat higher.

Judging from the absorption of brown glass at 1000 – 1100 nm its Fe^{2+} content is higher than in white and green glass, which is explained by the higher concentration of total iron introduced into the glass as a component and by the reducing conditions of glassmaking, which intensify the reduction of iron to Fe^{2+} .

Therefore, in order of increasing reducing potential the glass studied form the following series: brown > white > green.

Pellets were pressed to study the proneness of cullet to foam up from ground mixes whose composition is presented in Table 2. For each pellet, after heat-treatment at 1200°C for 30 min, the apparent density ρ_{app} was calculated from the expression (4) and the relative change Δ of the apparent density was calculated from Eq. (15):

$$\rho_{\text{app}} = \frac{m}{0.25\pi d^2 h}, \quad (14)$$

where m is the pellet mass, g; d is the pellet diameter, cm; h is the pellet height, cm;

$$\Delta = \frac{\rho_{\text{app1}} - \rho_{\text{app2}}}{\rho_{\text{app2}}} \times 100\%, \quad (15)$$

where ρ_{app1} and ρ_{app2} are the apparent densities of pellets prepared from mixed and single color cullet.

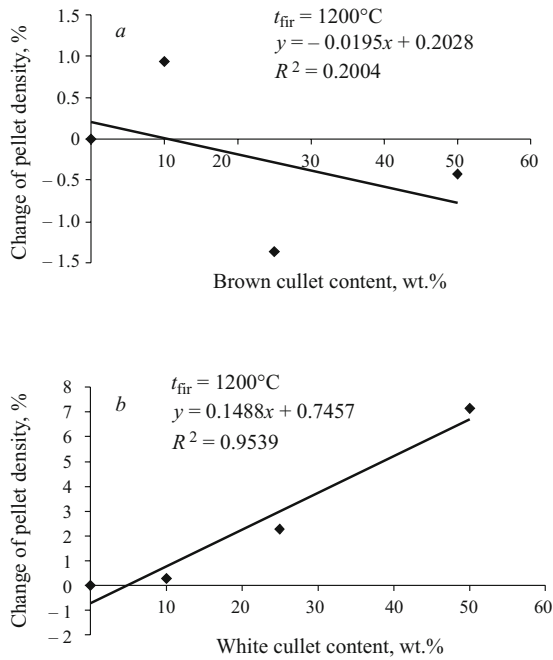


Fig. 3. Relative change of the apparent density of pellets prepared from green cullet with additives: a) brown and b) white cullet.

In accordance with the assumptions adopted in this work, a decrease of the apparent density of a pellet shows that it foams up intensively. An increase of ρ_{app} occurs as a result of sintering and shrinkage of the pellet.

The computational results are presented in Table 3 and in Figs. 3 – 5.

It follows from Table 3 and Figs. 3a, 4, and 5b that the values of Δ for samples from a mixture of cullet with oxidizing (white or green) and reducing (brown) potential decrease.

Therefore the samples are prone to foaming up, since a sudden change of the oxidation-reduction potential of the green or white glass lowers the solubility of SO_3 [9]. Intense release of gases with release of SO_2 starts because the sulfides formed in the glass with a reducing potential react with the residual sulfate of the glass with an oxidative potential [9]:

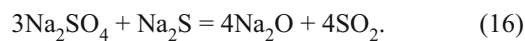


TABLE 3. Relative Change of the Apparent Density of Samples Heat-Treated at 1200°C

Mixture	Δ , %	Mixture	Δ , %
(G) 100%	0	(G) 100%	0
(G) 90%, (B) 10%	0.93	(G) 90%, (W) 10%	0.26
(G) 75%, (B) 25%	-1.36	(G) 75%, (W) 25%	2.25
(G) 50%, (B) 50%	-0.42	(G) 50%, (W) 50%	7.15
(B) 100%	0	(W) 100%	0
(B) 50%, (G) 50%	-0.74	(W) 50%, (G) 50%	7.52
(B) 50%, (W) 50%	-8.85	(W) 50%, (B) 50%	-8.24

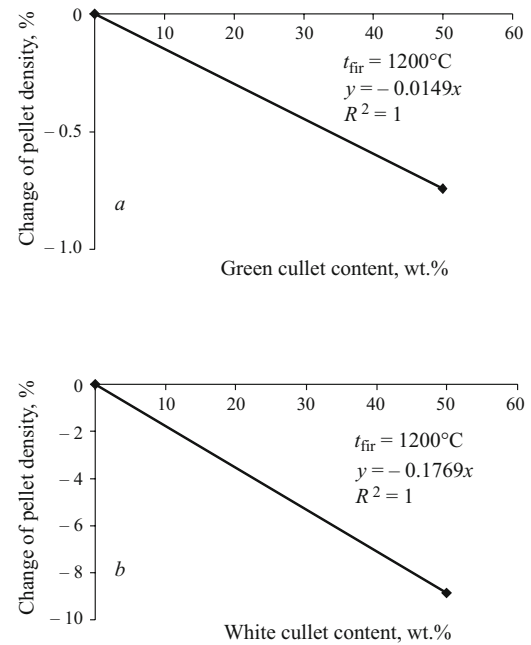


Fig. 4. Relative change of the apparent density of pellets prepared from brown cullet with additives: a) green and b) white cullet.

This phenomenon is not observed in samples from a mixture of cullet with oxidizing potential; here Δ increases as a result of sintering (Figs. 3b and 5a).

Glasses with a reducing potential are more sensitive to foaming than glass with an oxidizing potential. This follows from the steeper right-hand branch of the solubility curve for sulfur in Fig. 1. For this reason, it is observed that the de-

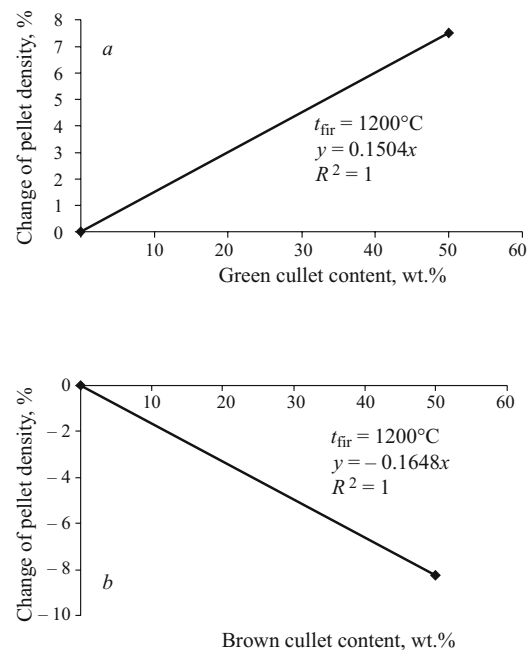


Fig. 5. Relative change of the apparent density of pellets prepared from white cullet with additives: a) green and b) brown cullet.

crease of the relative apparent density of brown glass to which green glass (– 0.74%) or white glass (– 8.85%) is added is larger than when brown glass is added to green (– 0.42%) and white (– 8.24%) glass (see Table 3).

In summary, the fining processes are closely related with oxidation-reduction potential of the glass. The appearance of seeds in optical glasses is due to the elevated solubility of nitrogen in melts with an elevated reducing potential. Adding cullet with an increased reducing potential to molten container glass with an oxidizing potential and vice versa destroys the solubility of sulfur and increases the risk of seeds appearing and the molten glass foaming up.

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